Supporting Information

Branched Polymeric Media: Boron-Chelating Resins from Hyperbranched Polyethyleneimine

Environmental Science and Technology

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The supporting information (SI) provides a detailed description of all the methods and procedures that were used to synthesize the new resins described in this study. The SI also includes supporting tables and figures.

I. Chemicals and Materials

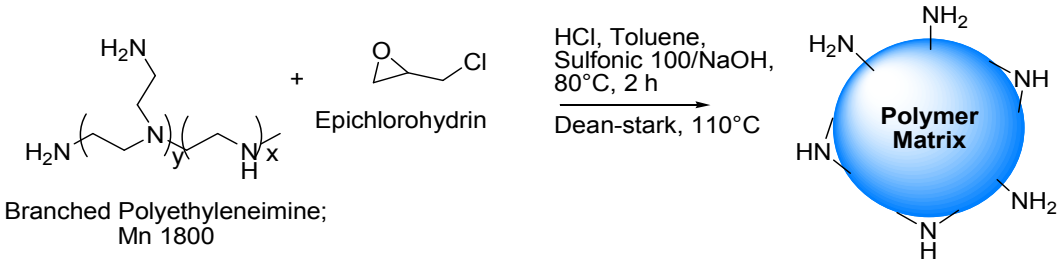
Reagent grade (> 98 wt%) anhydrous potassium chloride (KCl), sodium chloride (NaCl), sodium sulfate (Na_2SO_4) and ACS grade (99.5%) boric acid were purchased from Alfa Aesar. Concentrated hydrochloric acid (12 M) was purchased from EMD. The precursor polyethyleneimine macromolecules (PEI) [SP-018 (molecular weight M_n = 1800) and SP-200 (M_n = 10,000)] were purchased from Nippon Shokubai Co., Ltd. Sulfonic 100 (branched dodecyl benzene sulfonic acid, 97%) was purchased from the Stepan Company. Reagent grade (≥99.0%) D-Glucono-1,5-lactone, 1-bromo-3-chloropropane, diisopropyl ethylamine (DIPEA) and epichlorohydrin were purchased from Sigma-Aldrich. Methanol, ethanol, toluene, sodium bicarbonate ($NaHCO_3$), calcium chloride dihydrate ($CaCl_2$-$2H_2O$), magnesium chloride hexahydrate ($MgCl_2$-$6H_2O$), and sodium hydroxide (NaOH) were purchased from Mallinckrodt Chemicals. Deionized (DI) water was obtained from a Milli-Q filtration unit (minimum resistivity 18MΩ). All chemicals were used as received. The styrene-divinylbenzene (STY-DVB) Amberlite IRA-743 resin, which was specifically designed to remove boric acid and borate from water, was purchased from the Dow Chemical Company (Midland, MI, USA).

II. Materials Synthesis

All the PEI resins were synthesized and functionalized at AquaNano, LLC in Monrovia, CA, USA. The base PEI resins were synthesized using an inverse suspension of water-in-toluene stabilized by a surfactant. These were subsequently functionalized to produce resins containing boron-chelating vicinal diol groups. The synthetic procedures and corresponding reaction schemes are described below.

*II.1.Preparation of base PEI resin (***BPEI-1***)*

Reaction Scheme for **BPEI-1**

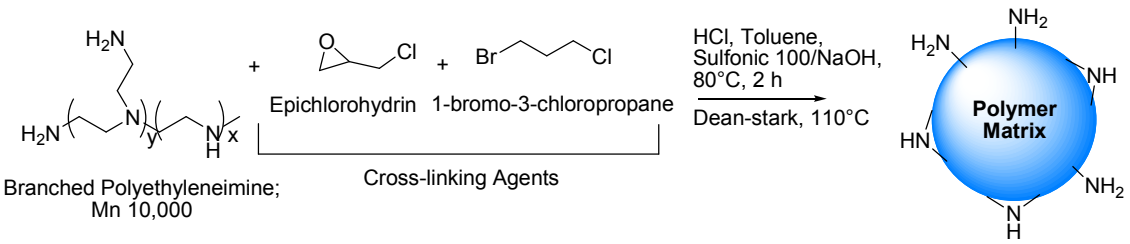


Equipment: Chemglass 1L Morton-type round bottom flask equipped with a mechanical stirrer, a thermometer, a reflux condenser, an addition funnel, and an inert gas port.

Recipe for **BPEI-1**: A solution of 43 g of HCl (36-38 % solution) in 69 g of DI water was added to the reaction flask containing 50 g of PEI over a course of 10 min at room temperature under nitrogen. Then a solution of 4 mg of surfactant [Sulfonic 100 + 1.1 M NaOH] was added to the vessel, followed by the addition of 450 mL of toluene. The oil bath temperature was then brought to 80 °C. In a separate vessel, 35 g of a solution of ECH in toluene (40 wt%) was prepared. The ECH solution was slowly added to the reaction mixture over a 60 min period. The reaction was continued for an additional 2 h. Following this, the dehydration of the reaction mixture was initiated using a Dean stark apparatus at a temperature of 110 °C. The reaction end point was reached when all the water from the system had been removed. After cooling to ambient temperature, the **BPEI-1** beads were collected by filtration over a Büchner funnel. The beads were then washed with methanol and a solution of NaOH (20 wt%) to remove the surfactant. Following this, the beads were sequentially washed with DI-water, NaCl (5 wt%) and DI water. The beads were then filtered off and stored at room temperature.

*II.2. Preparation of base BPEI resin (***BPEI-2***)*

Reaction Scheme for **BPEI-2**

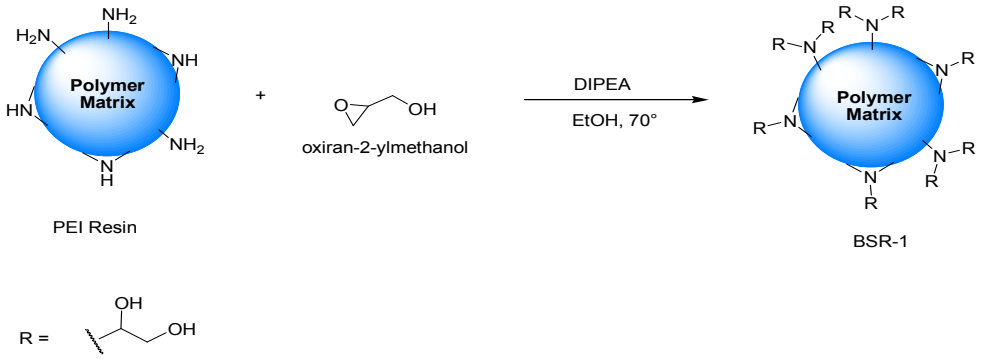


Equipment: ChemGlass 1L Morton-type round bottom flask equipped with a mechanical stirrer, a thermometer, a reflux condenser, an addition funnel, and an inert gas port.

Recipe for **BPEI-2**: A solution of 86 g of HCl (36-38 % wt solution) in 138 g of DI water was added to the reaction flask containing 100 g of PEI over a course of 10 min at room temperature under nitrogen. Then a solution of 4 mg of surfactant [Sulfonic 100 + 1.1 M NaOH] was added to the vessel, followed by the addition of 450 mL of toluene. The oil bath temperature was then brought to 80 °C. In a separate vessel, a toluene solution (40 wt%) containing 50 g of epichlorohydrin (ECH) and 100 g of 1-bromo-3-chloropropane (BCP) was prepared. The ECH/BCP solution was added to the reaction mixture over a 60 min period. The reaction was continued for an additional 2 h. Following this, the dehydration of the reaction mixture was initiated using a Dean stark apparatus at a temperature of 110 °C. The reaction end point was reached when all the water from the system had been removed. After cooling to ambient temperature, the **BPEI-2** beads were collected by filtration over a Büchner funnel. The beads were then washed with methanol and a solution of NaOH (20 wt%) to remove the surfactant. Following this, the beads were sequentially washed with DI-water, NaCl (5 wt%) and DI water. The beads were then filtered off and stored at room temperature.

II.3. Preparation of boron selective resin 1 **(BSR-1).**

Reaction Scheme for **BSR-1**

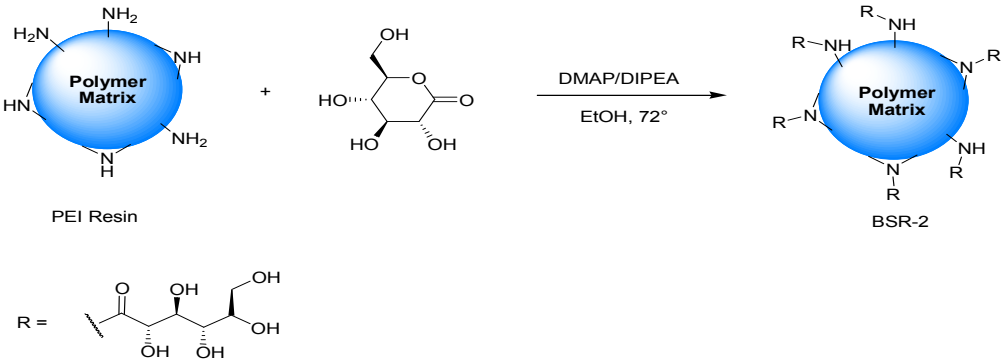


Recipe for **BSR-1**: 50 mL of ethanol (EtOH) was added into a 250 mL pressure vessel containing 25 g of Büchner dried **BPEI-1** beads. Then 30 g of oxiran-2-ylmethanol and 15 mL of diisopropyl ethylamine (DIPEA) [proton scavenger] was added to the mixture. The reaction mixture was stirred and heated to 70 °C in a temperature-controlled oil bath for 24 h to prepare the **BSR-1** beads. After cooling to room temperature, the beads were collected by filtration over a Büchner funnel and washed with methanol (MeOH) (1L/10g of resin) to remove organic reagents and byproducts. After rinsing with deionized water (1L/10g of resin),

the **BSR-1** beads were washed successively with 1.0 M HCl (1L/10g of resin), neutralized with 1.0 M NaOH (1L/10g of resin), and then washed with DI water until the pH of the eluate was neutral (~7.0).

II.4. Preparation of boron selective resin 2 **(BSR-2***).*

Scheme for **BSR-2**:



Recipe for **BSR-2**: 150 mL of ethanol (EtOH) was added into a 350 mL pressure vessel containing 50 g of Büchner dried **PEI-2**. Then 50 g of D-Glucono-1,5-lactone, 4 g of 4-Dimethylaminopyridine, and 15 mL of DIPEA was added to the mixture. The reaction mixture was stirred and heated to 72 °C in a temperature-controlled oil bath for 24 h to prepare the **BSR-2** beads. After cooling to room temperature, the beads were collected by filtration over a Büchner funnel and washed with methanol (MeOH) (1L/10g of resin) to remove organic reagents and byproducts. After rinsing with deionized water (1L/10g of resin), the **BSR-2** beads were washed successively with 1.0 M HCl (1L/10g of resin), neutralized with 1.0 M NaOH (1L/10g of resin), and then washed with DI water until the pH of the eluate was neutral (~7.0).

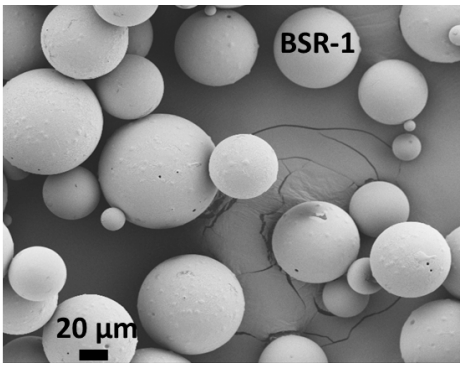
Table 1S. Composition of the Simulated Seawater RO Permeate [a]

Salt	Concentration (mM)
$CaCl_2$	0.008
$MgCl_2$	0.052
NaCl	2.12
KCl	0.058
$NaHCO_3$	0.012
Na_2SO_4	0.026

[a]The composition of the RO was based on a simulated seawater desalination RO permeate using using the software IMSDesign developed by Hydranautics (Available online at http://www.membranes.com/index.php?pagename=imsdesign).

Figure 1S: SEM Micrographs of the Boron-Selective PEI Resins.

A. BSR-1



B. BSR-2

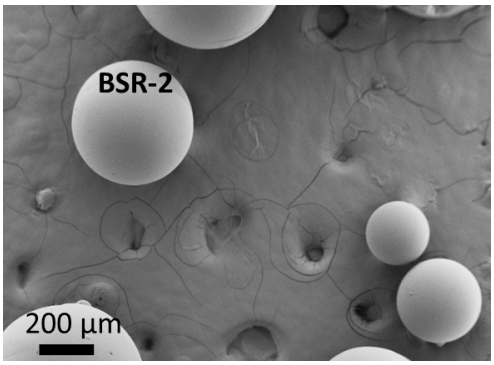


Figure 2S. Particle Size Distribution for the BSR-2 Resin.

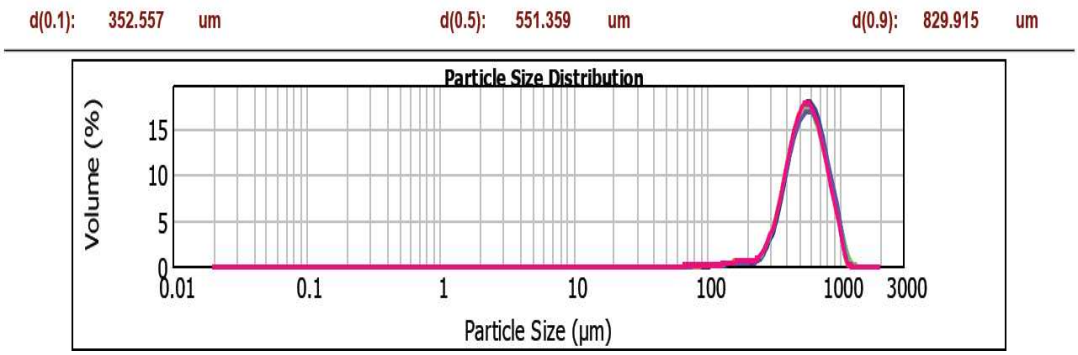


Figure 3S: Benchmarking the Titration Method by Comparing Target and Measured Boron Concentrations of a Series of Ten Samples in Deionized Water.

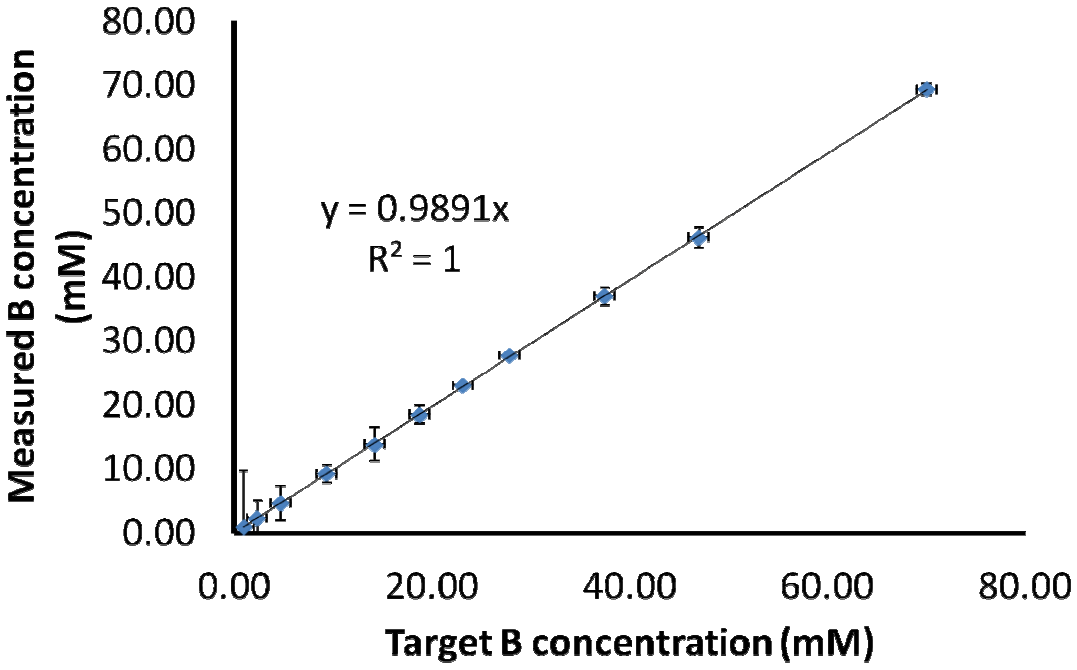
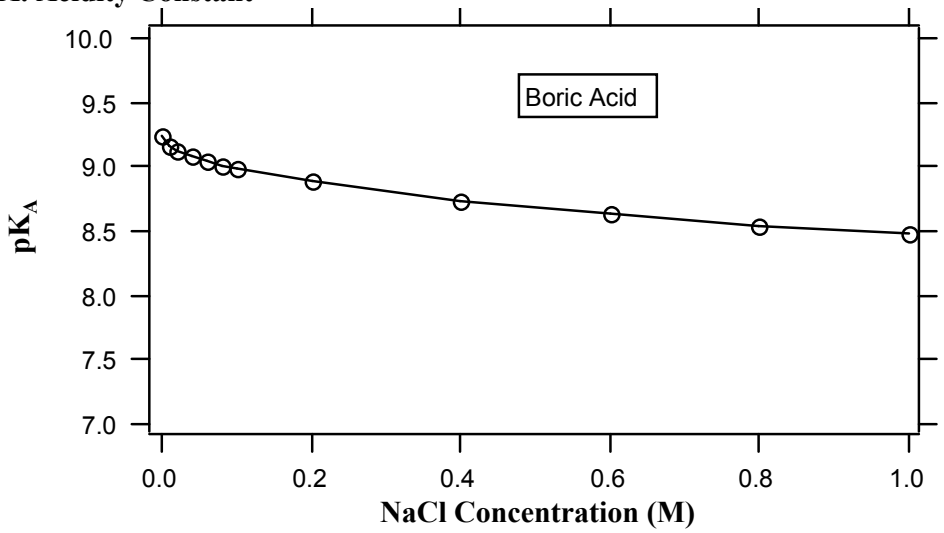
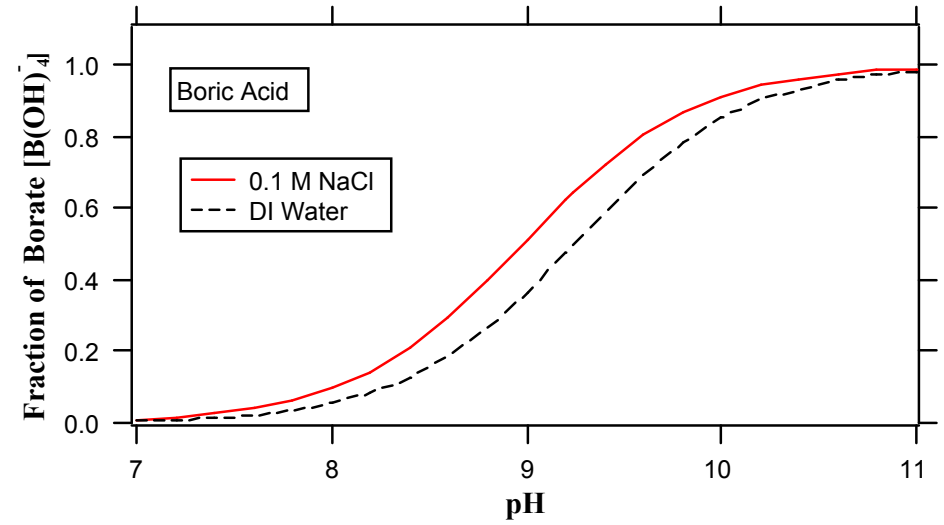


Figure 4S: Acidity Constant (A) and Speciation (B) of Boric Acid in Aqueous Solution of NaCl as a Function of Concentration at 25 °C. The pK_A data were taken from Hershey et al.[1] and used to determine the speciation of boric acid (e.g. fraction of borate versus pH) in a 0.1 M NaCl solution.

A. Acidity Constant



B. Speciation



[1] Hershey, J. P.; Fernandez, M.; Milne, P. J. and Millero, F. J. The ionization of boric acid in NaCl, Na-Ca-Cl and Na-Mg-Cl solutions at 25°C. *Geochimica et Cosmochimica Acta,* **1986**, 50, 143-148.